# Chemical Vapor Deposition

# Physical Vapor Deposition (PVD)

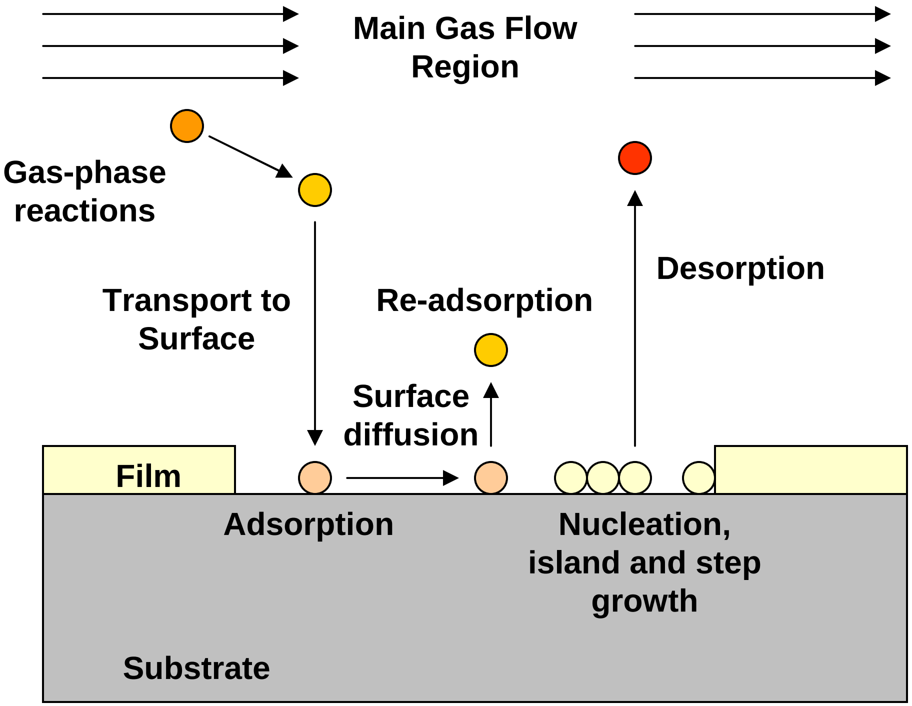
- So far we have seen deposition techniques that physically transport material from a condensed phase source to a substrate.
- The material to be deposited is somehow emitted from the source already in the form that we need for the thin film (ex.: evaporation, sputtering).
- No chemical reactions are assumed. In fact, they are generally unwanted. If there are chemical reactions (as in reactive sputtering) they are simple reactions with no by-products.
- The critical parameters are physical (temperature, pressure, voltage applied, etc.)

# Chemical Vapor Deposition (CVD)

- Deposition can also take place due to a chemical reaction between some reactants on the substrate.
- In this case reactant gases (precursors) are pumped in to a reaction chamber (reactor).
- Under the right conditions (T, P), they undergo a reaction at the substrate.
- One of the products of the reaction gets deposited on the substrate.
- The by-products are pumped out.
- The key parameters are chemical (reaction rates, gas transport, diffusion).

# Fundamental CVD Processes

1. Convective and diffusive transport of reactants to the reaction zone
2. Gas phase reactions
3. Transport of reactants to the substrate surface.
4. Chemical and physical adsorption
5. Surface reactions leading to film formation
6. Desorption of volatile by-products
7. Convective and diffusive transport of by-products away from the reaction zone



# CVD reactors

**Control module**

**Four reaction chambers**
(similar to those for Si oxidation)

**Control *T*, gas mixture, pressure, flow rate**

# Choice of Chemical Reactions

- The precursors have to be volatile (gaseous).
  - Ex: $SiH_4$ (Silane) is a popular precursor to deposit Silicon.
- The chemical reactions need to be thermodynamically predicted to result in a solid film.
  - This means that there should be an energy advantage for the desired reaction to occur, meaning the Gibbs Free Energy (GFE) has to decrease.
  - T and P can be adjusted for $\Delta G < 0$.
- The by-products need to be volatile (gaseous).

# More on GFE

- GFE is a measure of the total available energy in a system.
- If the overall GFE of the reactants is greater than the overall GFE of the products, that reaction is thermodynamically favorable.
- The equations relating the GFEs also determine the reaction rates.
- All of these quantities are affected by temperature and pressure.

# CVD Reaction Types - I

- Pyrolysis
  - Thermal decomposition of gaseous species on hot substrates.

$$SiH_4(g) \rightarrow Si(s) + 2H_2(g)$$ at 650 °C

$$Ni(CO)_4(g) \rightarrow Ni(s) + 4CO(g)$$ at 180 °C

  - Also can deposit, Al, Ti, Pb, Mo, Fe, B, Zr, C, Si, Ge, $SiO_2$, $Al_2O_3$, $MnO_2$, BN, $Si_3N_4$, GaN, $Si_{1-x}Ge_x$
- Reduction
  - Use hydrogen gas to reduce halides, carbonyl halides and oxyhalides

$$SiCl_4(g) + 2H_2 \rightarrow Si(s) + 4HCl(g)$$ at 1200 °C

$$WF_6(g) + 3H_2 \rightarrow W(s) + 6HF(g)$$ at 300 °C

  - Also can deposit, $Al_2O_3$, $TiO_2$, $Ta_2O_5$, $SnO_2$, ZnO

# CVD Reaction Types - II

- Oxidation
  - Using oxygen gas to produce oxides.

$$SiH_4(g)+O_2 \rightarrow SiO_2(s)+2H_2(g)$$ at 450 °C

$$2AlCl_3(g)+3H_2+3CO_2 \rightarrow Al_2O_3(s)++3CO+6HCl(g)$$

  - Also can deposit $TiO_2$, $Ta_2O_5$, $SnO_2$, ZnO
- Compound Formation
  - A variety of carbide, nitride and boride films can be formed.

$$SiCl_4(g)+CH_4 \rightarrow SiC(s)+4HCl(g)$$

$$BF_3(g)+NH_3 \rightarrow BN(s)+4HF(g)$$

# CVD Reaction Types - III

- Disproportionation
  - A solid metal can be deposited when there exists two valence states for a metal with different stable temperatures.
  - Requires mass transfer between hot and cold ends.

$$2GeI_2(g) \underset{600^\circ C}{\overset{300^\circ C}{\Leftrightarrow}} Ge(s) + GeI_4(g)$$

- Reversible Transfer
  - Depending on the temperature, you can get deposition or etching

$$As_4(g) + As_2(g) + 6GaCl(g) + 3H_2 \underset{850^\circ C}{\overset{750^\circ C}{\Leftrightarrow}} 6GaAs(s) + 6HCl(g)$$

# Nucleation

- In addition to being thermodynamically favorable, the barrier to nucleation (creating a nucleus increases surface energy) has to be overcome.
- Two types of nucleation exist:
  - Homogenous: Nuclei are formed in vapor form before being deposited and do not incorporate into the crystal structure of the film.
  - Heterogeneous: Nuclei are formed on the substrate and incorporate into the film structure more easily.

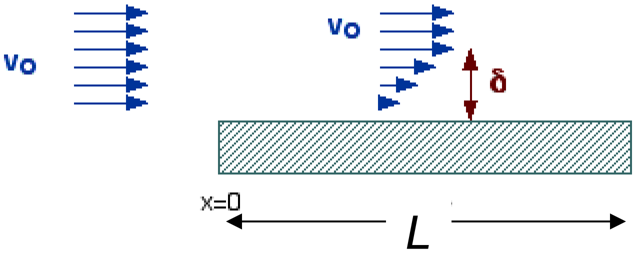
# Gas Transport

- This is the flow of the reactants through the CVD chamber.
- The goal is to deliver the gas uniformly to the substrate.
- The flow needs to be optimized for maximum deposition rate.
- Flow can be molecular (gas diffusion) or viscous (liquid flow).
- CVD takes place in the viscous regime.
  - ($Kn < 1$)
- In the viscous regime:
  - Low flow rates produce laminar flow (desired).
  - High flow rates produce turbulent flow (avoided).

# Boundary Layer

- While most flow in the chamber is laminar viscous flow, near the substrate surface the velocity of the gas has to go to zero.
- This creates a stagnant layer above the substrate.
- The thickness of this layer ($\delta$) depends on the chamber conditions.
- The gas will move through the layer by diffusion.

# Boundary Layer Gas Flow



$$\bar{\delta} = \frac{10}{3}\frac{L}{\sqrt{\mathrm{Re}_L}}$$

average width of stagnant layer

where Re is the Reynolds number of the flow tube and is a measure of the flow type.
For most CVD reactors: $\mathrm{Re}_L$ ~ few hundred
If flow is turbulent: $\mathrm{Re}_L$ ~ few thousand

$$D = D_0 \frac{P_0}{P}\left(\frac{T}{T_0}\right)^n$$

diffusion constant

where n is experimentally found to be 1.8 and $D_0$ is the diffusion constant at $T_0$ and $P_0$.

$$J_i = -\frac{D\left(P_g - P_s\right)}{\delta RT}$$

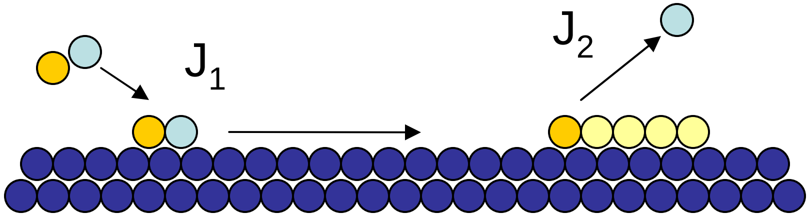
gas flow rate

where $P_g$ is the vapor pressure in bulk gas and $P_s$ is the vapor pressure is the substrate surface.

# Film Deposition

- In a simplified model, as gas flows over the substrate film growth is determined by adsorption and reaction rates.
- However, in reality, the deposition rate is affected by:
  - Distance from gas inlet
  - Specifics of the reaction
  - Radial variance
- Tricks to improve film uniformity:
  - Tilt substrate into flow
  - Increase T along the substrate
  - Single wafer processing

# Deposition Rate



$$J_1 = h_G\left(C_g - C_s\right)$$

$$J_2 = k_S C_s$$

$J_1$: Flux to surface
$J_2$: Reaction flux
$C_g$: Gas concentration
$C_s$: Concentration on surface

$h_g$: Gas phase mass transport coefficient
$k_s$: Surface reaction rate

In steady state $J_1 = J_2$ $\longrightarrow$ $$\boxed{v = \frac{C_g}{\frac{1}{h_G} + \frac{1}{k_S}}}$$ : deposition rate

# Limiting Cases

$$\boxed{v = \frac{C_g}{\frac{1}{h_G} + \frac{1}{k_S}}}$$

Two limiting cases:

- $h_G \gg k_S$ : Reaction Limited Growth
- $k_S \gg h_G$ : Transport Limited Growth

# Reaction Limited Growth

- growth controlled by processes on surface
  - adsorption
  - decomposition
  - surface migration
  - chemical reaction
  - desorption of products
- $k_S$ is highly temperature dependent (increases with T)
- common limit at lower temperatures
- often preferred, slow but epitaxial growth
- temperature and reactant choices are important

# Mass Transport Limited Growth

- growth controlled by transfer to substrate
- $h_G$ is not very temperature dependent
- common limit at higher temperatures
- non-uniform film growth
- gas dynamics and reactor design are important

# Summary

- Advantages:
  - high growth rates possible
  - can deposit materials which are hard to evaporate
  - good reproducibility
  - can grow epitaxial films
- Disadvantages
  - high temperatures
  - complex processes
  - toxic and corrosive gasses